

# Chapter 2

## Classical Models

In this Chapter we will discuss models that can be described by classical statistical mechanics. We will concentrate on the classical spin models which are used not only to study magnetism but are valid also for other systems like binary alloys or lattice gases.

In principle, all particles obey quantum statistical mechanics. Only when the temperature is so high and the density is so low that the average separation between the particles is much larger than the thermal wavelength  $\lambda$ ,

$$\left(\frac{V}{N}\right)^{1/3} \gg \lambda, \text{ where } \lambda = \left(\frac{\hbar^2}{2\pi mk_B T}\right)^{1/2}, \quad (2.1)$$

the quantum statistical mechanics reduces to classical statistical mechanics and we can use a classical, Maxwell-Boltzmann distribution function (instead of Fermi-Dirac or Bose-Einstein).

For magnetic materials, the situation is somewhat different. The Hamiltonian of a magnetic system is a function of spin operators which can usually not be directly approximated by classical vectors. Quantum models in  $d$  dimensions can be mapped onto classical models in  $d' = (d + 1)$  dimensions. The classical limit of the Heisenberg model, however, can be constructed for large eigenvalues of the spin operator by replacing the spin operators by three-dimensional classical vectors.

There is another quantum-mechanical effect we must discuss. In quantum mechanics identical particles are indistinguishable from each other whereas in classical mechanics they are distinguishable. Therefore, the partition function of a system of non-interacting, non-localized particles (ideal gas!) is not just the product of single-particle partition functions, as one would expect from classical statistical

mechanics, but we must take into account that the particles are indistinguishable. We must divide the total partition function by the number of permutations between  $N$  identical particles,  $N!$ ,

$$Z_N = \frac{1}{N!} (Z_1)^N, \quad (2.2)$$

where  $Z_1$  is the one-particle partition function. The factor  $N!$  is a purely quantum effect and could not be obtained from classical statistical mechanics.

In (insulating) magnetic systems we deal with *localized* particles (spins) and permutations among particles are not possible. Therefore we must not divide the partition function by  $(N!)$ .

A Hamiltonian of a simple magnetic system is:

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{i,j} \hat{\vec{S}}_i \hat{\vec{S}}_j - \vec{H} \sum_i \hat{\vec{S}}_i. \quad (2.3)$$

The first term is the interaction energy between the spins,  $J_{i,j}$  being the (exchange) interaction energy between the spins at the sites  $i$  and  $j$ . The sum is over all *bonds* between the spins.  $\hat{\vec{S}}$  is the spin operator; in general it is a vector. The *order parameter* is equal to the thermal and quantum-mechanical average of  $\hat{\vec{S}}$ ,  $\vec{m} = \langle \langle \hat{\vec{S}} \rangle \rangle$ . The thermal average of the first term in Eq. (2.3) is  $E(\mathcal{S}, \vec{m}) = \langle E(\mathcal{S}, \{S\}) \rangle$ . (Here,  $\mathcal{S}$  is the entropy and  $\{S\}$  is a spin configuration. The thermal average has to be taken over all spin configurations.)  $E(\mathcal{S}, \vec{m})$  is the *internal energy* of a magnetic system.

The second term in (2.3) is the interaction with external magnetic field  $\vec{H}$ . The thermal average of this term corresponds to  $PV$  in fluids. We see that  $\langle \mathcal{H}(\mathcal{S}, \vec{H}) \rangle$  is a Legendre transformation of  $E(\mathcal{S}, \vec{m})$  and is thus equivalent to the enthalpy of fluids.

## 2.1 Real Gases

In the ideal gas we neglected the collisions between the particles. In reality, the atoms (molecules) have a finite diameter and when they come close together, they *interact*. The Hamiltonian of interacting particles in a box is:

$$\mathcal{H} = \sum_i \left[ \frac{\vec{p}_i^2}{2m} + U(\vec{r}_i) \right] + \sum_{i>j} u(r_i - r_j), \quad (2.4)$$

$u(r_i - r_j) = u(r)$  is the interaction energy and  $U$  the potential of the box walls. The particles are polarizable and this leads to an attractive van der Waals interaction between the induced electric dipole moments. Such an interaction energy is proportional to  $r^{-6}$ , where  $r$  is the interatomic distance. At short distances, however, the electrons repel because of the Pauli exclusion principle. Although the repulsive potential energy usually decays exponentially with  $r$ , we will write it in the form:

$$u(r) = \begin{cases} \infty & r < 2r_0 \\ -\epsilon(2r_0/r)^6 & r > 2r_0 \end{cases} \quad (2.5)$$

( $2r_0$  is the minimal distance to which the particles of "hard-core" radius  $r_0$  can approach.)

The partition function of  $N$  interacting identical particles is

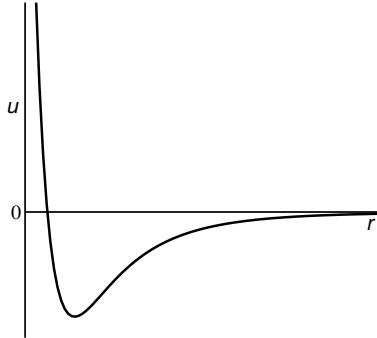


Figure 2.1: Interatomic potential energy  $u(r)$  in real gases.

$$Z(T, V, N) = \frac{1}{h^{3N} N!} \int \cdots \int d^3 p_1 \cdots d^3 p_N \int \cdots \int d^3 r_1 \cdots d^3 r_N \times e^{-\beta [\sum_i (p_i^2/2m + U) + \sum_{i>j} u(r_{i,j})]} \quad (2.6)$$

After integrating over all momenta, the partition function becomes:

$$Z(T, V, N) = \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} Z_I(T, V, N), \quad (2.7)$$

where  $Z_I$  carries all the interactions between the particles. We calculate the partition function in a mean-field approximation in which all the correlations are neglected. The potential acting on one particle is calculated by assuming a uniform

spatial distribution of other particles,

$$Z_I = \left[ \int_0^{V_1} d^3 r_1 e^{-\beta \Phi} \right]^N \quad (2.8)$$

$V_1$  is the volume, available to one particle,  $V_1 = V - (N/2)(4\pi/3)(2r_0)^3 = V - Nb$ . Here we subtracted from  $V$  the volume occupied by other particles.  $N/2$  is the number of pairs of particles. The mean-field potential  $\Phi$  is:

$$\Phi = - \int_{2r_0}^{\infty} \epsilon (2r_0/r)^6 (N/V) 4\pi r^2 dr = - \frac{2Na}{V} \quad (2.9)$$

The resulting partition function is

$$Z(T, V, N) = \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} (V - Nb)^N e^{\beta N^2 a / V} \quad (2.10)$$

( $a = (2\pi/3)\epsilon (2r_0)^3$ ,  $b = (2\pi/3)(2r_0)^3$ ), the Helmholtz free energy is:

$$F(T, V, N) = -k_B T \ln Z = -N k_B T \ln \left[ \frac{V - Nb}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] - \frac{N^2 a}{V}, \quad (2.11)$$

and the equation of state is

$$p(T, V, N) = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{N k_B T}{V - Nb} - \frac{N^2 a}{V^2}. \quad (2.12)$$

The last equation can be written in a more familiar form:

$$(p + \frac{N^2 a}{V^2})(V - Nb) = N k_B T. \quad (2.13)$$

This is the familiar *van der Waals equation*. We derived the van der Waals equation of state in a mean-field approximation, we neglected all the correlations between the molecules. Nevertheless, this equation qualitatively correctly describes the liquid-gas transition and it also predicts the existence of the critical point. However, as we neglected the correlations, which are essential in the vicinity of the critical point, it does not predict the correct critical behaviour.

The critical point is located at the inflexion point of the isotherm,  $(\partial p / \partial V)_T = (\partial^2 p / \partial V^2)_T = 0$ , and is located at:

$$\begin{aligned} V_C &= 3Nb \\ p_C &= \frac{a}{27b^2} \\ T_C &= \frac{8a}{27bk_B} \end{aligned} \tag{2.14}$$

Below the critical point, the liquid and the gas phases are separated by a first-order phase transition. The *equilibrium* transition between the two phases takes place when their chemical potentials and therefore the Gibbs free energies are equal.

Some comments are in place here.

- *Critical exponents.* The van der Waals equation was derived in a mean-field approximation, therefore all the exponents are mean-field like.
- *Liquid → gas transition.* The liquid phase is stable until the point *A* is reached. In equilibrium, at this point, liquid starts to evaporate, the system enters the *coexistence region* (mixture of gas and liquid) until the point *B* is reached, which corresponds to the pure gas phase.

If equilibrium is not reached, the liquid phase persists beyond the point *A* towards the point *D*. In this region, the liquid is *metastable* and can (at least in principle) persist until the point *D* is reached. Beyond this point, the compressibility is negative, the liquid state is *unstable* (not accessible).

- *Gas → liquid transition.* The situation is reversed. In equilibrium, the gas phase is stable until the point *B* is reached. This is the onset of the coexistence region which exists until the point *A* is reached. Metastable gas phase exists between the points *B* and *E* and, again, the region *E* to *D* is unstable.
- Convexity. As we have discussed in Section 2.3.3 already, the Helmholtz free energy *F* of a stable system has to be a concave function of *V*. For metastable states it is concave *locally* whereas for unstable states, it is convex.

- *Spinodals.* The transition from a metastable (homogeneous) state toward the equilibrium (mixed) state is connected with the *nucleation of droplets of the new phase*. Droplets first nucleate and then grow until the equilibrium (coexistence) is reached between the new and the old phase. Nucleation is a dynamic process.

The ultimate stability limit of the metastable state is called the spinodal line. Along this line the isothermal compressibility diverges, therefore the spinodal line is in a sense a line of critical points. In the van der Waals (mean-field) systems the separation between the metastable and unstable states is sharp. Beyond MFA, for systems with short-range correlations, however, the transition between metastable and unstable states is often gradual.

## 2.2 Ising Model

The Ising model is the prototype model for all magnetic phase transitions and is probably the most studied model of statistical physics. In this model, the spin operator  $\hat{S}$  is replaced by a *number*, which represents the  $z-$  component of the spin and is usually  $S = \pm 1$  ("up" or "down"). The order parameter  $m = \langle S \rangle$  is thus *one-dimensional*, it is a *two-component scalar*.

The Ising Hamiltonian is

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j - H \sum_i S_i \quad (2.15)$$

$J_{ij}$  is the interaction energy between the spins  $i$  and  $j$ . Usually (not always) the sum is only over nearest neighbouring (NN) pairs, then  $J_{ij} = J$ .  $H$  is the external magnetic field (in energy units). The case  $J > 0$  corresponds to ferromagnetism and  $J < 0$  to antiferromagnetism. As we shall show later, the Ising model has a phase transition at finite  $T$  if  $d > 1$ . In  $d = 1$  the transition is at  $T = 0$ . Therefore we say that  $d = 1$  is the *lower critical dimension* of the Ising model.

In the low-temperature phase, the symmetry is broken, the spins are *ordered*, the order parameter is  $m \neq 0$ , whereas in the high-temperature phase the symmetry is not broken,  $m$  vanishes, the spins are disordered. Therefore this model is a prototype of all *order-disorder* transitions. Other examples of order-disorder transitions, I would like to mention, are lattice gases and binary alloys. All these systems are equivalent to each other, they all have the same critical behaviour (which - of course - depends on  $d$ ), for given  $d$  they all belong to the same universality class.

### 2.2.1 Lattice Gas

Imagine that a fluid (gas or liquid) system is divided into a regular lattice of cells of volume roughly equal to the particle (atom, molecule) volume. We say that the cell is occupied if a particle centre falls into this cell. Since the cell volume is comparable to the particle volume, there can be not more than one particle per cell. Notice that microscopic details (like positions of the particles) are irrelevant in the critical region, therefore the lattice gas model is suitable for studying the critical behaviour of real gases although the space is discretized. (It is also assumed that the kinetic energy of the gas particles, which is neglected in the lattice gas model, does not contribute a singular part to the partition function.)

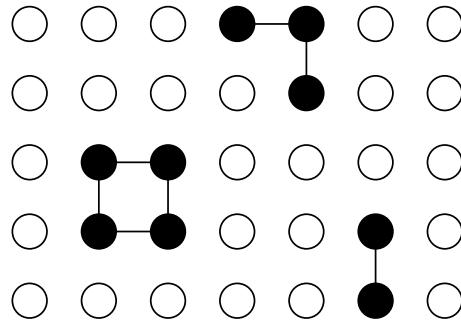


Figure 2.2: A configuration of a lattice gas in  $d = 2$ . Solid circles represent atoms and open circles empty sites. Lines show bonds between nearest-neighbouring atoms.

A lattice gas is thus a collection of particles whose kinetic energy is neglected and that are arranged into *discrete* cells. The cells are either occupied by one atom [closed circles in Fig. 2.2] or empty [open circles]. The Hamiltonian is:

$$\mathcal{H}_{lg} = \sum_{\langle i,j \rangle} u(r_{i,j}) p_i p_j - \mu \sum_i p_i, \quad (2.16)$$

where  $u$  is the interaction potential,

$$u(r_{i,j}) = \begin{cases} \infty & (r_{i,j} = 0) \\ -u & (r_{i,j} = \text{NN distance}) \\ 0 & (\text{otherwise}) \end{cases} \quad (2.17)$$

and  $\langle i,j \rangle$  is the sum over pairs.  $p_i$  is the occupation number, it is 1 if the site is occupied by an atom, and zero otherwise. The occupation is, like the Ising spin,

a double-valued function. Therefore we expect that the two models are related. Indeed, if we set

$$p_i = \frac{1 + S_i}{2}, \quad (2.18)$$

the Hamiltonian 2.16 becomes:

$$\mathcal{H}_{lg} = -\frac{u}{4} \sum_{\langle i,j \rangle} S_i S_j - \left( \frac{\mu}{2} + \frac{uz}{4} \right) \sum_i S_i - \mathcal{H}_0. \quad (2.19)$$

Here,  $z$  is the number of NN neighbours (4 for square lattice, 6 for simple cubic lattice), and  $\mathcal{H}_0$  is a constant, independent of  $S$ . Thus, we see that  $\mathcal{H}_{lg}$  is identical to the Ising Hamiltonian if we set  $u/4 = J$  and  $(\mu/2 + uz/4) = H$ . For  $u > 0$ , the atoms attract and they "condense" at low temperatures whereas for  $u < 0$  the atoms repel. At 1/2 coverage (one half of the lattice sites is occupied) and  $u < 0$ , the empty and occupied sites will alternate at low  $T$ , like spins in an antiferromagnet.

The lattice gas model in  $d = 2$  is used to investigate, e.g., hydrogen adsorbed on metal surfaces. The substrate provides discrete lattice sites on which hydrogen can be adsorbed. By varying the pressure, the coverage (amount of adsorbed hydrogen) is varied. This corresponds to varying the field in magnetic systems.

There is an important difference between the lattice gas and the Ising models of magnetism. The number of atoms is constant (provided no atoms evaporate from or condense on the lattice), we say that the order parameter in the lattice gas models is *conserved* whereas it is not conserved in magnetic systems. This has important consequences for dynamics.

### 2.2.2 Binary Alloys

A binary alloy is composed of two metals, say A and B, arranged on a lattice. We introduce the occupations:

$$\begin{aligned} p_i &= \begin{cases} 1 & \text{if } i \text{ is occupied by an A atom} \\ 0 & \text{if } i \text{ is occupied by a B atom} \end{cases} \\ q_i &= \begin{cases} 1 & \text{if } i \text{ is occupied by a B atom} \\ 0 & \text{if } i \text{ is occupied by an A atom} \end{cases} \\ p_i + q_i &= 1. \end{aligned} \quad (2.20)$$

Depending on which atoms are nearest neighbours, there are three different NN interaction energies:  $u_{AA}$ ,  $u_{BB}$ , and  $u_{AB} = u_{BA}$ . The Hamiltonian is:

$$\mathcal{H}_{ba} = -u_{AA} \sum_{\langle i,j \rangle} p_i p_j - u_{BB} \sum_{\langle i,j \rangle} q_i q_j - u_{AB} \sum_{\langle i,j \rangle} (p_i q_j + q_i p_j), \quad (2.21)$$

where each sum  $\langle i,j \rangle$  runs over all NN pairs. If we write  $p_i = (1 + S_i)/2$  and  $q_i = (1 - S_i)/2$  then  $S_i = 1$  if  $i$  is occupied by A and  $S_i = -1$  for a B site. When there are 50% A atoms and 50% B atoms,  $\sum_i S_i = 0$ , and the Hamiltonian becomes an Ising Hamiltonian in the absence of a magnetic field:

$$\mathcal{H}_{ba} = -J \sum_{\langle i,j \rangle} S_i S_j + \mathcal{H}_0. \quad (2.22)$$

$\mathcal{H}_0$  is a constant, and  $J = (u_{AA} + u_{BB} - 2u_{AB})/4$ . For binary alloys, the order parameter is also conserved.

### 2.2.3 Ising model in $d = 1$

It is not difficult to solve the Ising model in the absence of  $H$  in  $d = 1$  exactly. The Hamiltonian of a linear chain of  $N$  spins with NN interactions is

$$\mathcal{H}_{1d} = -J \sum_i S_i S_{i+1}. \quad (2.23)$$

We shall use *periodic boundary conditions*, that means that the spins will be

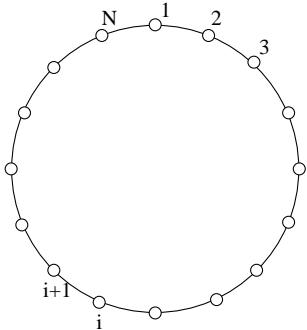


Figure 2.3: Lattice sites of an Ising model in one dimension with periodic boundary conditions.

arranged on a ring, see Fig. 2.3. Then, the  $N$ -th and the first spins are NN and the system is periodic. The partition function is:

$$Z = \sum_{\{S\}} e^{-\beta \mathcal{H}(\{S\})} = \sum_{\{S\}} e^{\beta J \sum_i S_i S_{i+1}} = \sum_{\{S\}} \prod_{i=1}^N e^{\beta J S_i S_{i+1}}. \quad (2.24)$$

(Don't forget:  $\sum_{\{S\}}$  is the sum over all spin *configurations* – there are  $2^N$  spin configurations – whereas  $\sum_i$  is the sum over all *sites*!)

The exponent in (2.24) can be written as:

$$e^{\beta J S_i S_{i+1}} = \cosh \beta J S_i S_{i+1} + \sinh \beta J S_i S_{i+1} = \cosh \beta J + S_i S_{i+1} \sinh \beta J. \quad (2.25)$$

The last equality holds because  $S_i S_{i+1}$  can only be  $\pm 1$  and  $\cosh$  is an even function whereas  $\sinh$  is an odd function of the argument. The partition function is:

$$Z = (\cosh \beta J)^N \sum_{\{S\}} \prod_{i=1}^N [1 + K S_i S_{i+1}], \quad (2.26)$$

where  $K = \tanh \beta J$ . We work out the product and sort terms in powers of  $K$ :

$$\begin{aligned} Z &= (\cosh \beta J)^N \sum_{\{S\}} (1 + S_1 S_2 K)(1 + S_2 S_3 K) \cdots (1 + S_N S_1 K) \\ &= (\cosh \beta J)^N \sum_{\{S\}} [1 + K(S_1 S_2 + S_2 S_3 + \cdots + S_N S_1) + \\ &\quad + K^2(S_1 S_2 S_3 + \cdots) + \cdots + K^N(S_1 S_2 S_3 \cdots S_N S_N S_1)]. \end{aligned} \quad (2.27)$$

The terms, linear in  $K$  contain products of two different (neighbouring) spins, like  $S_i S_{i+1}$ . The sum over all spin configurations of this product vanish,  $\sum_{\{S\}} S_i S_{i+1} = 0$ , because there are two configurations with parallel spins ( $S_i S_{i+1} = +1$ ) and two with antiparallel spins ( $S_i S_{i+1} = -1$ ). Thus, the term linear in  $K$  vanishes after summation over all spin configurations. For the same reason also the sum over all spin configurations, which appear at the term proportional to  $K^2$ , vanish. In order for a term to be different from zero, all the spins in the product must appear twice (then,  $\sum_{\{S_i\}} S_i^2 = 2$ ). This condition is fulfilled only in the last term, which – after summation over all spin configurations – gives  $2^N K^N$ . Therefore the partition function of the Ising model of a linear chain of  $N$  spins is:

$$Z = (2 \cosh \beta J)^N [1 + K^N]. \quad (2.28)$$

In the thermodynamic limit,  $N \rightarrow \infty$ ,  $K^N \rightarrow 0$ , and the partition function becomes:

$$Z(H = 0) = (2 \cosh \beta J)^N. \quad (2.29)$$

The free energy,

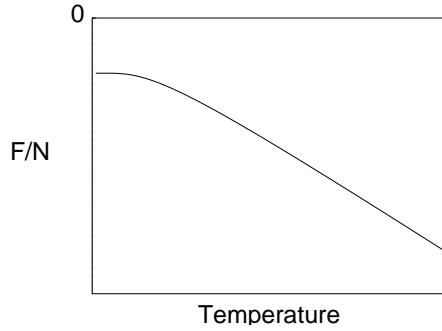


Figure 2.4: Free energy of the Ising model in  $d = 1$ .

$$F = -Nk_B T \ln(2 \cosh \beta J), \quad (2.30)$$

is regular at all finite  $T$ , therefore the Ising model in  $d = 1$  has no phase transition at any finite  $T$ .

To investigate the possibility of a phase transition at  $T = 0$ , we will calculate the correlation function  $\Gamma$  and the correlation length  $\xi$ . We first replace  $J$  by  $J_j$  (at the end we put  $J_j = J$ ), so that

$$Z = 2^N \prod_j \cosh \beta J_j. \quad (2.31)$$

The nearest-neighbour spin-spin correlation function is:

$$\begin{aligned} \Gamma(i, i+1) &= \langle S_i S_{i+1} \rangle = \frac{1}{Z} \sum_{\{S\}} S_i S_{i+1} e^{\beta \sum_j J_j S_j S_{j+1}} \\ &= \frac{1}{\beta Z} \frac{\partial Z}{\partial J_i} = \tanh(\beta J_i). \end{aligned} \quad (2.32)$$

The spin correlation function for arbitrary distance  $k$ ,

$$\Gamma(i, i+k) = \langle S_i S_{i+k} \rangle$$

$$= \frac{\langle S_i S_{i+1} S_{i+2} S_{i+3} S_{i+k-1} S_{i+k-2} S_{i+k} \rangle}{Z \frac{\partial}{\partial(\beta J_i)} \frac{\partial}{\partial(\beta J_{i+1})} \frac{\partial}{\partial(\beta J_{i+2})} \cdots \frac{\partial}{\partial(\beta J_{i+k-1})} Z}, \quad (2.33)$$

$$\Gamma(k) \equiv \Gamma(i, i+k) = [\tanh(\beta J)]^k, \quad (2.34)$$

is just the product of all the nearest-neighbour correlation functions between the sites  $i$  and  $i+k$ , and is (if all  $J$ 's are equal) independent of the site  $i$ . The decay of the spin correlation function with distance is shown in Fig. 2.5. The correlations decay exponentially with distance and the correlation length is:

$$\frac{\xi}{a} = -\frac{1}{\ln \tanh \beta J}, \quad (2.35)$$

where  $a$  is the separation between the NN spins ("lattice constant"). In the limit  $T \rightarrow 0$ , the correlation length diverges exponentially as  $T \rightarrow 0$ :

$$\frac{\xi}{a} \approx \frac{1}{2} e^{2\beta J}. \quad (2.36)$$

Equations 2.34 and 2.36 tell us that there is no long range order at any finite  $T$  and

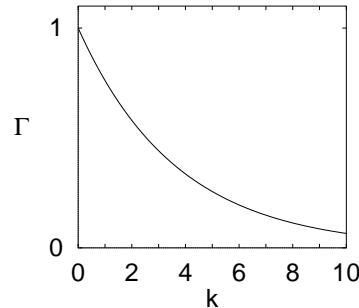


Figure 2.5: Decay of the correlations in the  $d = 1$  Ising model.

that  $T = 0$  is the critical temperature of the  $d = 1$  Ising model. Such a behaviour is typical for systems in the lower critical dimension:

$$d > d_C : \quad T_C \neq 0 \quad (2.37)$$

$$d \leq d_C : \quad T_C = 0, \quad (2.38)$$

therefore we conclude that  $d = 1$  is the *lower critical dimension* of the Ising model.

The zero-field isothermal susceptibility of the  $d = 1$  Ising model is, according to the fluctuation-dissipation theorem,

$$\chi_T(H=0) = \frac{\beta}{N} \sum_{i,j} \langle S_i S_j \rangle. \quad (2.39)$$

In the thermodynamic limit,  $\chi_T$  becomes:

$$\begin{aligned} \chi_T(H=0) &= \frac{\beta}{N} \sum_i \sum_{k=-N/2}^{N/2} \langle S_i S_{i+k} \rangle \\ &= \frac{\beta}{N} \sum_i \left[ 2 \sum_{k=0}^{N/2} \langle S_i S_{i+k} \rangle - \langle S_i S_i \rangle \right]. \end{aligned} \quad (2.40)$$

In the thermodynamic limit ( $N \rightarrow \infty$ ),  $\chi_T(H=0)$  becomes

$$\chi_T(H=0) = \beta \left[ \frac{2}{1 - \tanh \beta J} - 1 \right] = \frac{1}{k_B T} e^{2J/k_B T}. \quad (2.41)$$

The susceptibility has an essential singularity of the type  $\exp(1/T)$  as  $T \rightarrow T_C = 0$  when  $J > 0$ . When  $J < 0$ , i.e., for antiferromagnetic NN interaction, the spin correlation function alternates in sign and the susceptibility is finite at all  $T$ .

The internal energy is:

$$E = -\partial \ln Z / \partial \beta = -JN \tanh \beta J. \quad (2.42)$$

Notice the similarity between the internal energy and the short-range correlation function  $\Gamma(i, i+1)$ ! This is a general property of the internal energy.

The entropy is  $S = (E - F)/T$ ,

$$S(H=0) = Nk_B \ln [2 \cosh \beta J] - \frac{NJ}{T} \tanh \beta J. \quad (2.43)$$

In the limit  $T \rightarrow 0$ ,  $S \rightarrow 0$  and in the limit  $T \rightarrow \infty$ ,  $S \rightarrow Nk_B \ln 2$ , see Fig. 2.6.

The heat capacity  $C_H = T(\partial S / \partial T)_H$  is:

$$C_H = Nk_B \left( \frac{\beta J}{\cosh \beta J} \right)^2. \quad (2.44)$$

The heat capacity is finite at all temperatures (no singularity at  $T = 0$ !), see Fig. 2.7.

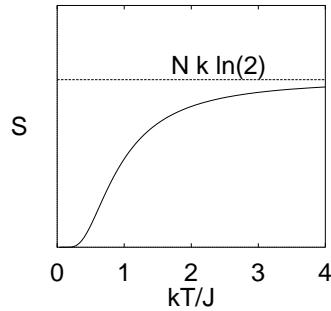


Figure 2.6: Temperature dependence of the entropy for the zero-field  $d = 1$  Ising model.

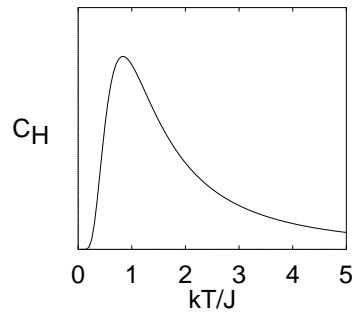


Figure 2.7: Temperature dependence of the heat capacity for the zero-field  $d = 1$  Ising model.

### 2.2.4 Ising Model in $d = 2$

The Ising model for  $H = 0$  in  $d = 2$  dimensions has been solved exactly by Onsager. The calculation is lengthy, therefore we will first show that the Ising model in  $d = 2$  has a phase transition at finite  $T$  and then quote the Onsager's result.

Consider a two-dimensional square lattice with all the spins on the outer boundary "up". This simulates an arbitrarily weak external field and breaks the up-down symmetry of the model. To show that spontaneous ordering exists, it is enough to show that in the thermodynamic limit at a sufficiently small but finite temperature there are more spins "up" than "down". Now we will estimate the fraction of "down" spins from the average size of a spin-down domain.

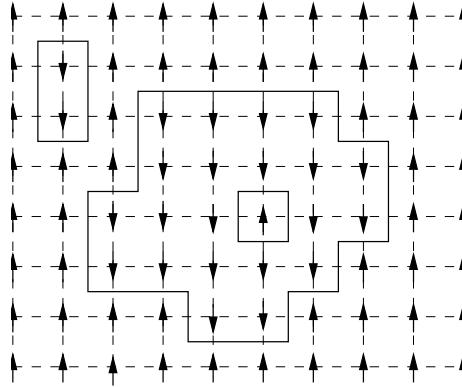


Figure 2.8: A possible domain configuration of the Ising model on a square lattice.

With the above boundary conditions, all the domain walls must be closed loops, see Fig. 2.8. In a wall the neighbouring spins are antiparallel, this costs an energy  $2J$  per wall segment and the probability, that a domain with its total wall length (perimeter)  $b$  is thermally excited, is given by the Boltzmann factor  $\exp[-2\beta Jb]$ . For large  $b$ , there are many possible domain wall configurations with the same wall length  $b$ . For an estimate of the number  $m$  of possible wall configurations, assume that on each site the wall can either be straight or make a kink to either side. This makes a factor of 3 for each wall segment (except for the last one where it is bound to close the loop). Besides, a wall can start on each lattice site, this makes a factor of  $N$ . Therefore,  $m(b)$  is limited by:

$$m(b) \leq 3^{b-1} N \quad (2.45)$$

and the average number of different thermally excited domains with perimeter  $b$  is:

$$\leq 3^{b-1} N e^{-2\beta Jb}. \quad (2.46)$$

The number of "down" spins in a domain with perimeter  $b$  is  $N_- \leq (b/4)^2$  and the average concentration of all "down" spins is:

$$\begin{aligned} \frac{\langle N_- \rangle}{N} &\leq \sum_{b=4,6,8,\dots} \frac{b^2}{16} 3^{b-1} e^{-2\beta Jb} \\ &= \frac{1}{48} \frac{\partial^2}{\partial \alpha^2} \sum_{b=4,6,8,\dots} 3^b e^{-\alpha b} \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{48} \frac{\partial^2}{\partial \alpha^2} \sum_{x=2,3,4,\dots} (9e^{-2\alpha})^x \\
&= \frac{1}{48} \frac{\partial^2}{\partial \alpha^2} \left( \frac{q^2}{1-q} \right) \\
&= \frac{q^2(4-3q+q^2)}{12(1-q)^3}, 
\end{aligned} \tag{2.47}$$

where  $\alpha = 2\beta J$ ,  $x = 2b$ ,  $q = 9 \exp(-2\alpha)$ . For large, finite  $\beta$ ,  $q$  is small and the above ratio is  $< 1/2$ . This means that the order parameter  $\langle N_+ - N_- \rangle / N$  is greater than zero at low  $T$  and the Ising model in  $d = 2$  (and of course also in  $d > 2$ ) has a phase transition at finite  $T$ .

The exact critical temperature of the (anisotropic) Ising model on a rectangular lattice is given by the equation:

$$\sinh\left(\frac{2J_x}{k_B T_C}\right) \sinh\left(\frac{2J_y}{k_B T_C}\right) = 1,$$

where  $J_x$  and  $J_y$  are the spin interaction energies in  $x$  and  $y$  directions, respectively.

## 2.3 Potts and Related Models

In the previous Section we have discussed different classical two-state models (which are all mapped on the Ising model). A large class of classical physical systems cannot be described by the Ising model. As an example consider adsorption of noble gases on surfaces, like krypton on graphite. Graphite provides a two-dimensional hexagonal lattice of adsorption sites. Kr is large and once it occupies one hexagon, it is unfavourable for another Kr atom to occupy any of its NN hexagons, see Fig. 2.9. At full coverage, thus, Kr forms a regular lattice with 1/3 of hexagons covered by Kr. Since there are three entirely equivalent positions (states!) for Kr (denoted by A, B, and C), the system is described by a three-state model. The adsorbed Kr forms A,B,C *domains*, separated by *domain walls*. It is clear from Fig. 2.9 that the A-B and the B-A walls are not equivalent, they have different energies in general.

In the Potts model there are  $q$  states available to each site. The Potts Hamiltonian (with only NN interactions) is:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \delta_{\sigma_i, \sigma_j}. \tag{2.48}$$

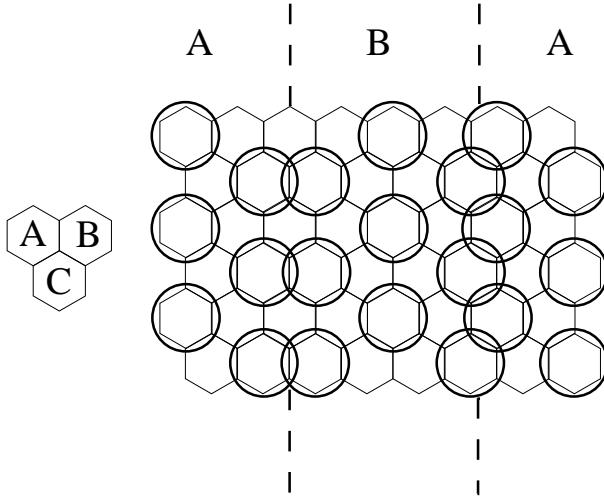


Figure 2.9: Kr on graphite. There are three equivalent adsorption sites, but Kr atoms are too big to occupy all of them – only one third of the sites (i.e., either "A," "B," or "C" sites) can be occupied. We talk about "A," "B," or "C" domains. The domains are separated by domain walls. The A-B domain wall has a different structure (and energy) than the B-A wall.

$J$  is the interaction energy and  $\delta_{\sigma_i, \sigma_j}$  is the  $\delta$ -function which is = 1 if the NN sites  $i$  and  $j$  are in the same *state* and zero otherwise,

$$\delta_{\sigma_i, \sigma_j} = \begin{cases} 1 & \sigma_i = \sigma_j \text{ with } (i, j) \in NN \\ 0 & \text{otherwise} \end{cases} \quad (2.49)$$

$\sigma_i = 1, 2, \dots, q$  is a number which describes the *state* of the site  $i$ . Thus, in the Potts model, the interaction energy is equal to  $-J$  if the two NN sites are in the same state and vanishes otherwise. For  $q = 2$ , the Potts model is equivalent to the Ising model ( $S = \pm 1$ ) because each site has two possible states in both cases. The two states can be visualized as two points on a line (which is a one-dimensional object). The mapping from the Potts to the Ising model is accomplished by writing:

$$\delta_{S_i S_j} = \frac{1 + S_i S_j}{2}. \quad (2.50)$$

For  $q = 3$  the three states of the Potts model can be visualized as corners of a triangle (which is a two-dimensional object) whereas for  $q = 4$ , the four states

belong to corners of a tetrahedron, which is a 3-dimensional object. We conclude that the order parameter of the  $q$ -state Potts model is a  $q$ -component scalar. In  $d = 2$ , the Potts model has a continuous phase transition for  $q \leq 4$  and a first-order transition for  $q > 4$ .

*Order parameter.* Let  $x_A, x_B, \dots, x_q$  be the fractions of cells (sites) that are in the states A, B,  $\dots$ ,  $q$ , respectively. Of course,  $x_A + x_B + \dots + x_q = 1$ . In the disordered phase, all the fractions are equal whereas in the ordered phase one state, say A, will have greater probability than the other,  $x_A > (x_B, x_C, \dots, x_q)$ . We make a simplified approach, assuming that  $x_B = x_C = \dots = x_q$ . The order parameter  $m$  measures the asymmetry in occupancies,

$$\begin{aligned} m &= x_A - \frac{x_B + \dots + x_q}{q-1} \\ x_A &= \frac{1 + (q-1)m}{q}, \quad x_B = x_C = \dots = x_q = \frac{1-m}{q} \end{aligned}$$

It is easy to verify that for  $m_A = 0$ :  $x_A = x_B = x_C = \dots = x_q$  and for  $m = 1$ :  $x_A = 1$  and  $x_B = x_C = \dots = x_q = 0$ . thus,  $m_A$  is the order parameter which is  $\neq 0$  in the ordered phase and vanishes in the disordered phase.

I would like to mention another generalization of the 2-state model, that is the  $q$ -state (chiral) clock model. In this model, the states are imagined as hands of a clock (i.e., vectors on a circle) that can take only discrete orientations,  $\Theta_i = (2\pi/q)\sigma_i$  (where  $\sigma_i = 0, 1, 2, \dots, q-1$ ). The  $q$ -state chiral clock Hamiltonian is

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \cos(\Theta_i - \Theta_j + \vec{\Delta} \cdot \vec{r}_{i,j}) \quad (2.51)$$

$\Delta$  is the chirality which breaks the symmetry of the model, it produces an asymmetry in the interaction between the NN sites. The interaction energies between, say,  $\sigma_i = 0, \sigma_j = 1$  and  $\sigma_i = 1, \sigma_j = 0$  are different. The two-state clock model is identical to the Ising model and, if  $\Delta = 0$ , the 3-state clock model is identical to the 3-state Potts model. For  $q > 3$ , the clock and the Potts model are not identical. The two-dimensional clock and Potts models are widely used in surface physics. The above mentioned Kr on graphite can be described with the 3-state chiral clock model with  $\Delta \neq 0$ .

## 2.4 Two-dimensional $xy$ Model

A very interesting situation appears when the spin is a continuous vector in a plane (dimensionality of the order parameter is 2) and the spatial dimensionality is also

$d = 2$ . As we have seen, the Ising model in  $d \geq 2$  does have a phase transition at finite  $T_C$ . In the  $xy$  model, however, spin excitations (spin waves) are easier to excite thermally than for the Ising model, they are so strong that they even destroy long-range order at any finite  $T$  (Mermin-Wagner theorem). On the other hand, there has been evidence that some kind of a transition does take place at a finite  $T_C$ . What is the ordering and what is the nature of this transition? This question was answered in the early seventies by Berezinskii and by Kosterlitz and Thouless.

The Hamiltonian of the  $xy$  model is:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j = -J \sum_{\langle i,j \rangle} \cos(\Phi_i - \Phi_j), \quad (2.52)$$

where the spins are classical vectors of unit length aligned in the plane.  $\Phi_i$  is the angle between the spin direction and an arbitrarily chosen axis and is a continuous variable. For simplicity, let us consider the square lattice and let the sum be only over nearest neighbours. Only slowly varying configurations ( $\Phi_i - \Phi_j \ll 1$ ) give considerable contributions to the partition function, therefore we expand  $\mathcal{H}$ :

$$\begin{aligned} \mathcal{H} - E_0 &= \frac{J}{2} \sum_{\langle i,j \rangle} (\Phi_i - \Phi_j)^2 = \frac{Ja^2}{2} \sum_i |\vec{\nabla}\Phi(i)|^2 \\ &= \frac{J}{2} \int d^2r |\vec{\nabla}\Phi(r)|^2. \end{aligned} \quad (2.53)$$

Here  $a$  is the lattice constant and we transformed the last sum over all lattice sites into an integral over the area.  $\Phi(r)$  is now a scalar field.

Possible excitations above the (perfectly ordered) ground state are spin waves. They are responsible for destroying long-range order at any finite  $T$ . We will not consider spin waves here. Another possible excitation above the ground state is a vortex, shown in Fig. 2.10. Any line integral along a closed path around the centre of the vortex will give

$$\oint \vec{\nabla}\Phi(\vec{r}) \cdot d\vec{r} = 2\pi q \quad \Rightarrow \quad \begin{cases} \Phi = q\phi \\ |\vec{\nabla}\Phi| = q/r \end{cases} \quad (2.54)$$

where  $q$  is the vorticity ( $q$  is integer;  $q = 1$  for the vortex shown in Fig. 2.10) and  $\phi$  is the polar angle to  $\vec{r}$ . From the equations (2.53) and (2.54) we find the energy of this vortex:

$$E = \int_a^R 2\pi r dr \frac{J}{2} \left(\frac{q}{r}\right)^2 = \pi J \ln\left(\frac{R}{a}\right) q^2. \quad (2.55)$$

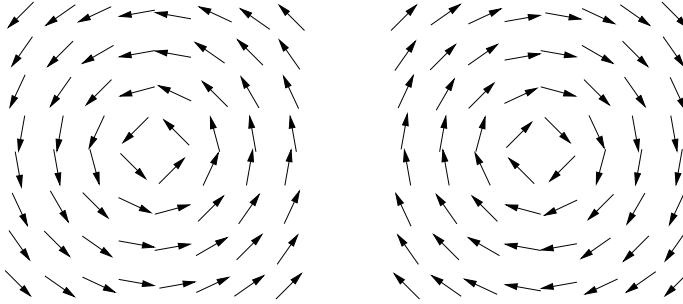


Figure 2.10: Two examples of a vortex with vorticity  $q = 1$ .

$R$  is the size of the system. Notice that the energy of the vortex increases logarithmically with the size of the system. In estimating the entropy associated with a vortex we realize that a vortex can be put on each lattice site therefore the number of configurations is about  $(R/a)^2$  and the entropy of one vortex is

$$S \approx 2k_B \ln \left( \frac{R}{a} \right). \quad (2.56)$$

The free energy,  $F = E - TS$ , is positive and large at low temperatures. That means that it is not very easy to (thermally) excite single vortices. As temperature increases, the entropy term causes  $F$  to decrease.  $F$  vanishes (changes sign) at a critical temperature:

$$k_B T_C = \frac{\pi J}{2}. \quad (2.57)$$

Above  $T_C$  a large number of vortices is thermally excited.

However, this does not mean that there are no vortices at low  $T$ . The easiest way to see this is to draw an analogy to a system of electrical charges in two dimensions. If  $\vec{k}$  is a unit vector perpendicular to the plane of the system, then  $\vec{\mathcal{E}} = \vec{\nabla}(q\phi) \times \vec{k}$  is equal to the electric field produced by a charge of strength  $2\pi\epsilon_0 q$  positioned at the centre of the vortex. The energy of an electric field is

$$E_{el} = \frac{\epsilon_0}{2} \int d^2r |\vec{\mathcal{E}}|^2 = \frac{\epsilon_0}{2} \int d^2r |\vec{\nabla}(q\phi) \times \vec{k}|^2, \quad (2.58)$$

whereas the energy of a system of vortices is

$$E_{vort} = \frac{J}{2} \int d^2r |\vec{\nabla}\Phi \times \vec{k}|^2 = \frac{J}{\epsilon_0} E_{el}. \quad (2.59)$$

The energy of a system of vortices of strength  $q_i$  is equivalent to the energy of a system of electric charges! There is almost a complete analogy between a system of vortices and the two-dimensional Coulomb gas. We have seen that, like the electrostatic energy of a single charge in two dimensions, also the energy of a vortex diverges logarithmically with the size of the system. However, a pair of opposite charges, i.e., a dipole does have a finite electrostatic energy because at large distances the fields of two opposite charges almost cancel. In analogy to the energy of two charges  $\pm q$  at  $\vec{r}_1$  and  $\vec{r}_2$  we write the total energy of a system of two opposite vortices:

$$E_{2 \text{ vort}} = 2\pi J q^2 \ln \left( \frac{|\vec{r}_1 - \vec{r}_2|}{a} \right). \quad (2.60)$$

This self-energy of a vortex pair (of a dipole) is very small when the vortices are close together. Thus, it is difficult to excite a single vortex but it is very easy to excite a pair of opposite vortices. Whereas a single vortex influences the spin configuration on the whole lattice, the effect of a pair of opposite vortices cancels out on large distances from the pair so that the effect is limited to an area of the order  $|\vec{r}_1 - \vec{r}_2|^2$ .

Since the size of the system does not appear in (2.60), but it does appear in the expression for the entropy, we will have a finite density of bound vortex pairs. The equilibrium density of vortex pairs will depend on the pair-pair (dipole-dipole in the Coulomb gas case) interaction which we neglected here.

Now we have the following picture. At low but  $> 0$  temperature ( $T < T_C$ ) there will be a finite density of low-energy vortex *pairs* ("dipoles") of zero total vorticity. At high temperatures ( $T > T_C$ ), on the other hand, there will be a large concentration of *single* vortices. The critical temperature, we estimated above, is thus associated with *unbinding (dissociation) of vortex pairs*.

Very interesting is the behaviour of the spin correlation function  $\langle \vec{S}_i \cdot \vec{S}_j \rangle$ . We already mentioned that spin-wave excitations break the long-range order. If we neglect the spin wave excitations (which have nothing to do with the phase transition, they do not behave in a critical way at any finite temperature), then:

$$\lim_{|\vec{r}_i - \vec{r}_j| \rightarrow \infty} \langle \vec{S}_i \cdot \vec{S}_j \rangle = \begin{cases} > 0 & \text{for } T < T_C \\ 0 & \text{for } T > T_C. \end{cases} \quad (2.61)$$

This follows from the fact that bound vortices don't influence the spin orientations at large distances whereas they do if they are free.

In a more realistic approach, one must take into account interaction between the vortex pairs, which was neglected in (2.60). Surrounding vortices (dipoles!) will screen the (electric) field and will thus reduce the self-energy of a vortex.

A sophisticated real-space renormalization group treatment of the two-dimensional  $xy$  model [Kosterlitz 1974] shows that the correlation length  $\xi$  diverges above  $T_C$  as:

$$\xi \propto \exp(b/t^{1/2}) \quad b \approx 1.5 \quad (2.62)$$

where  $t = (T - T_C)/T_C$ . Below  $T_C$ , however, the correlation length is always infinite and the correlations decay algebraically (like in a critical point)! Therefore we can say that we have a line of critical points extending from zero to  $T_C$ . The phase transition is characterized by a change from algebraic (power-law) decay of correlations below  $T_C$  to an exponential decay above  $T_C$ .

Analogous to vortex unbinding transition in the  $xy$  model is the unbinding of opposite charges of a dipole in the two-dimensional Coulomb gas. At low temperatures, the Coulomb gas is composed of neutral dipoles, bound pairs, and is not conducting. At high temperature it is composed of free + and - charges which are conducting.

Another analogy to the  $xy$  model are the dislocation lines in a (three-dimensional) crystal. At low temperatures, pairs of dislocation lines with opposite Burgers vectors can exist. At  $T_C$ , the dislocations dissociate. This is the basis of the dislocation theory of melting. In this latter example, stiffness can play the role of the order parameter, it is  $\neq 0$  below the melting temperature and vanishes in the liquid phase.

Let me stress again that the described behaviour of Coulomb gases or  $xy$  systems is specific only for *two-dimensions*!

## 2.5 Spin Glasses

The (vitreous) glasses are amorphous materials, their lattice is not crystalline but is strongly disordered. Topological defects destroy the long-range order in the crystalline structure whereas the short-range order is still preserved to a high degree. Example: topological defects on a square lattice would be triangles or pentagons. Of course, the defects cause also a deformation of the squares.

Spin glasses are the magnetic (spin) analogue of the (vitreous) glasses. In magnetic systems, the exchange interaction is often an oscillating function of distance between the spins. If such a system is diluted with non-magnetic ions, the magnetic atoms are randomly positioned on the lattice and thus experience random exchange interactions with other, neighbouring atoms. Example:  $\text{Au}_{1-x}\text{Fe}_x$ , where  $x$  is small.

Another system, which behaves in a similar way, is a random mixture of a ferromagnetic and an antiferromagnetic materials. The exchange interaction between nearest neighbours  $i$  and  $j$  is random, it depends on the type of the magnetic atoms  $i$  and  $j$ .

A Hamiltonian which reflects the essential features of a spin glass is:

$$\mathcal{H} = - \sum_{i,j} J(R_{i,j}) \vec{S}_i \cdot \vec{S}_j - \sum_i \vec{H} \cdot \vec{S}_i. \quad (2.63)$$

$J(R_{i,j})$  is a random variable and the first sum includes also more distant pairs than just nearest neighbours. Random exchange interactions cause that – even at low temperatures – the spins are not ordered, the system has *no long-range order in the ground state*. The “usual” long-range order parameter

$$m = \frac{1}{N} \sum_i \langle S_i \rangle \quad (2.64)$$

vanishes for a spin glass. Yet, in the experiment, a broad maximum in the specific heat and a rather sharp maximum in the zero-field susceptibility, connected with hysteresis and remanescence, are seen. So, there must be a kind of a transition as the temperature is varied, we shall call this a spin-glass transition and the low-temperature state the spin-glass phase.

At high temperatures, the spins behave like in a normal paramagnet, they flip around dynamically so that the thermodynamic average  $\langle S_i \rangle$  vanishes. There is no long-range order in the system and also the local spontaneous magnetization, i.e., the (time) average of the spin at a site  $i$  vanishes,  $\langle S_i \rangle = 0$  for each site. At low temperatures, however, the spins *freeze* in a disordered configuration, the system is in a state where  $\langle S_i \rangle \neq 0$  although the average magnetization still vanishes,  $m = 0$ . The spin-glass transition is thus a freezing transition.

Something happens to the dynamics of the spins, therefore we must consider time-dependent spins,  $S(t)$ . To distinguish between the two phases, we introduce the (Edwards-Anderson) order parameter:

$$q = \lim_{t \rightarrow \infty} \lim_{N \rightarrow \infty} \frac{1}{N} \sum_i \langle S_i(t_0) S_i(t_0 + t) \rangle. \quad (2.65)$$

$q$  clearly vanishes in the paramagnetic phase and is  $> 0$  in the spin-glass phase, see Fig. 2.12. It measures the mean square local spontaneous magnetization. Notice that freezing is a gradual process, which starts at  $T_f$  where the first spins freeze and ends at  $T = 0$  where all the spins are frozen.

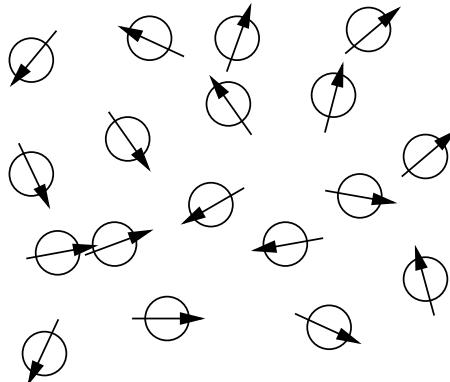


Figure 2.11: Spins in the low-temperature, spin-glass phase are frozen in a disordered configuration.

Since, in the spin-glass phase the spins are (at least partially) frozen in a disordered configuration, we can easily imagine that some spins are frustrated and that the spins do not freeze in a unique way. Freezing is history dependent, the configuration into which the spins freeze, depends on the conditions (e.g, on the magnitude of the magnetic field) close to the freezing temperature. If we, upon cooling, apply an external field pointing "up", there will be more spins frozen in the "up" orientation and will stay in this orientation even if we switch the field off in the low-temperature phase. This means that the systems can fall into a metastable configuration from which it is not able to escape if the temperature is low. The free energy, thus, has many, many local minima in the *configuration space*, see Fig. 2.13. In the thermodynamic limit ( $N \rightarrow \infty$ ), some hills between the local minima will become infinitely high and the system will be trapped in such a minimum forever. In the time average, thus, the system will explore only a part of the total configuration space. This means that the *time average* of a physical quantity is no longer equal to the *ensemble average* (where one explores the whole configuration space). A system in *the spin-glass phase* is thus *not ergodic* in the thermodynamic limit! Since it is ergodic in the paramagnetic phase, we say that at the freezing transition the ergodicity breaks down.

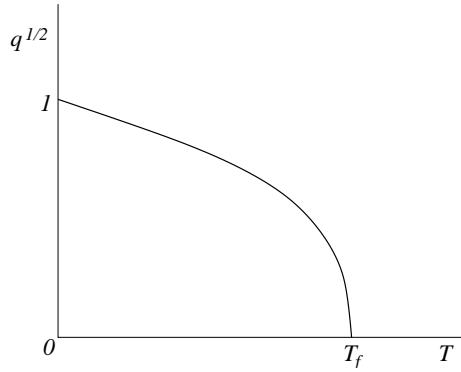


Figure 2.12: Temperature dependence of the order parameter  $q$ . Upon cooling, the spins start to freeze at  $T_f$ ; below  $T_f$ , more and more spins are frozen until, eventually, at  $T = 0$  all the spins are frozen.

### 2.5.1 Some Physical Properties of Spin Glasses

The static susceptibility, Fig. 2.14, below the freezing temperature depends strongly on the way the experiment is performed.  $\chi(T)$  is largest and roughly temperature independent in a "field cooling" (FC) cycle, i.e., if the field  $H$  is applied above  $T_f$  and then the sample is cooled at constant  $H$  below  $T_f$ . This susceptibility is reversible, it is independent of the history. In contrast, the "zero-field cooled" (ZFC) susceptibility is obtained if the sample is cooled to  $T \approx 0$  at  $H = 0$  and then the sample heated in the field. The difference between  $\chi_{FC}$  and  $\chi_{ZFC}$  confirms the conjecture that the system can be frozen in different spin configurations (which, of course, also have different susceptibilities).

The conjecture that freezing takes place at  $T_f$  is confirmed also by the *ac* susceptibility measurements, shown in Fig 2.15 for  $\text{Cu}_{1-x}\text{Mn}_x$  ( $x = 0.9\%$ ) at different frequencies. The lower the frequency, the more pronounced (less rounded) the cusp is. We see also that the position of the cusp shifts to lower temperatures as the frequency decreases. So, the freezing temperature should be defined as the maximum of  $\chi(\nu)$  in the limit as  $\nu \rightarrow 0$ .

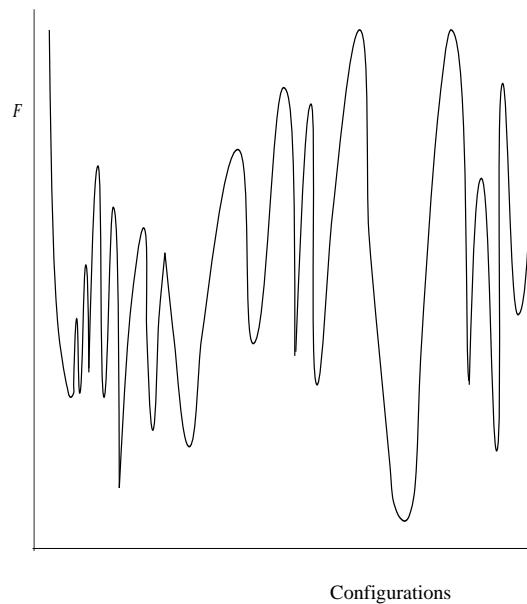


Figure 2.13: Free energy landscape in the configuration space of a spin glass at low temperatures. There is one global and many local minima.

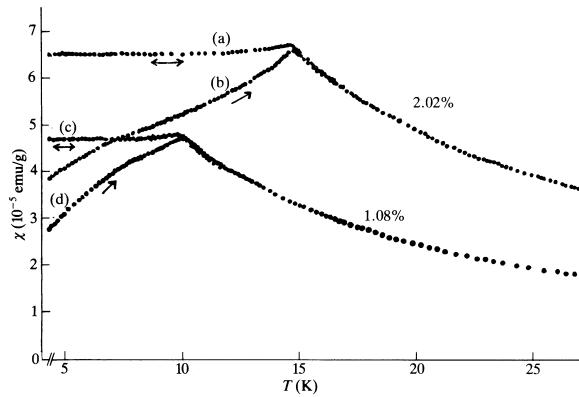


Figure 2.14: Temperature dependence of the static susceptibility of  $\text{Cu}_{1-x}\text{Mn}_x$  for  $x = 1.08$  and  $2.02\%$ . (b) and (d): cooled to low temperature at  $H = 0$  and then heated at  $H = 5.9$  Oe; (a) and (c): cooled and/or heated in  $H = 5.9$  Oe. [From Nagata et al., Phys. Rev. B **19**, 1633 (1979).]

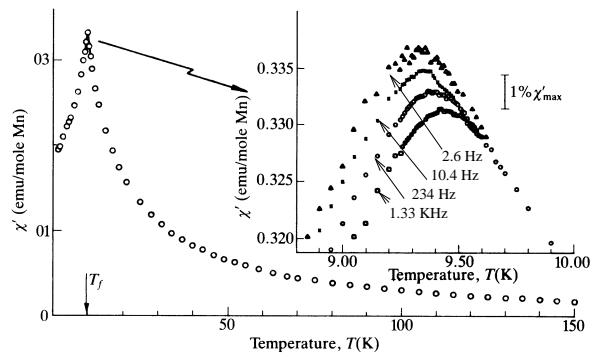


Figure 2.15: Temperature dependence of the frequency-dependent susceptibility of  $\text{Cu}_{1-x}\text{Mn}_x$  ( $x = 0.9\%$ ). [From C.A.M. Mulder et al., Phys. Rev. **B 23**, 1384 (1982), *ibid.* **25**, 515 (1982).]

